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This report describes the preparation of a third series of reference materials for the chemical analysis of natural precipitation samples. These materials were prepared by the National Bureau of Standards (NBS), under the joint sponsorship of the Environmental Protection Agency (EPA), and the U. S. Geological Survey (USGS), and will be used as a means of intercalibrating atmospheric monitoring stations. These materials consist of high and low concentrates which upon dilution simulate the range of anion and cation concentrations typically found in natural rainwater. Two separate reference samples which are to be used undiluted are provided for evaluation of acidity measurements. The analytical methods used to establish the composition of the samples are also described.

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SIMULATED PRECIPITATION REFERENCE MATERIALS, III

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ABSTRACT

This report describes the preparation of a third series of reference materials for the chemical analysis of natural precipitation samples. These materials were prepared by the National Bureau of Standards (NBS), under the joint sponsorship of the Environmental Protection Agency (EPA), and the U. S. Geological Survey (USGS), and will be used as a means of intercalibrating atmospheric monitoring stations. These materials consist of high and low concentrates which upon dilution simulate the range of anion and cation concentrations typically found in natural rainwater. Two separate reference samples which are to be used undiluted are provided for evaluation of acidity measurements. The analytical methods used to establish the composition of the samples are also described.

1. INTRODUCTION

The analysis of the composition of rainfall and other forms of precipitation is an excellent means to monitor global atmospheric pollution. Such measurements must necessarily be made at widely spaced geographical locations, over extended periods of time, and by many independent investigators. It is imperative that the measuring stations be intercalibrated if the data obtained are to be correlated and combined for environmental interpretation. The measurement of a series of substantially identical samples by stations in a measurement system is an accepted method of evaluating laboratory performance for intercalibration purposes.

This report describes work done at the National Bureau of Standards under the sponsorship of EPA to prepare and establish the composition of a series of reference materials intended to be used for the intercalibration of precipitation measurement stations[1]. The materials consist of

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[1]This work was performed at the National Bureau of Standards for the Environmental Protection Agency and the U. S. Geological Survey under Interagency Agreement EPA-79-D-F0666 and Purchase Order 84312, respectively.

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ampoules containing aqueous concentrates that simulate natural precipitation when accurately diluted. Two multi-component solutions and two solutions specifically designated for acidity measurement were prepared.

This is the third series of solutions prepared for EPA to be used by the World Meteorological Organization (WMO) stations. The details of the first and second series are contained in NBSIR 75-958, "Simulated Precipitation Reference Materials", October 1975, and NBSIR 77-1315 "Simulated Precipitation Reference Materials II", September 1977.

2. EXPERIMENTAL DETAILS

2.1 General Considerations

These reference materials are similar in concept to those prepared previously. Two reference solutions, low concentrations (Series 910000), and the other high concentrations (Series 920000) were prepared of specified components at levels similar to those expected in natural samples (Table 1). In addition, two reference materials (Series 930000, and Series 940000) containing 3 microequivalents (μeq) and 5 μeq of sulfuric acid, respectively, per ampoule are included specifically for the measurement of acidity.

2.2 Preparation of Reference Materials

The reference materials were prepared using distilled water whose specific conductance does not exceed 1 micro siemens per centimeter (1 μS/cm) at 25 °C and reagent grade chemicals. Distilled water in this report refers to this quality of water. The chemicals used and their sources are listed in Table 2. The quantities of chemicals are listed in Table 3.

The instructions for the preparation of Series 910000 and Series 920000 are as follows:

Ten liters of the required solutions can be prepared using the quantities of reagents set forth in the instructions supplied by EPA (Table 3). The procedure is as follows: Transfer the reagents with the exception of sodium fluoride and lead acetate using distilled water to a one liter volumetric flask and make up nearly to volume with distilled water. Because of its low solubility, add the sodium fluoride at this point and dilute to calibrated volume, Solution A. Transfer the lead acetate to another one liter volumetric flask and dilute to 800 mL. Add 100 mL of Solution A by pipet to the lead acetate solution and dilute to calibrated volume, Solution B.

Transfer by pipet 400 mL of Solution A to each of two volumetric flasks, four liter capacity, and make up to volume. Filter both four liter solutions and the one liter containing the lead acetate, Solution B, through a Whatman 40 filter paper into a ten liter ground glass stoppered bottle.

Series 930000 and Series 940000 were prepared by the dilution of an appropriate volume of 0.06N sulfuric acid to a final volume of 30 liters. The sulfuric acid solution was standardized using two different procedures. In the first, the acid was titrated against THAM (Tris(hydroxymethyl) aminomethane) SRM 723. In addition, the acid was also titrated against a 0.05N sodium hydroxide solution that had been previously standardized with potassium acid phthalate, SRM 84h.

2.3 Ampouling

The bulk solutions were transferred to ampoules using an automatic dispensing and sealing machine belonging to the Office of Standard Reference Materials. The ampoules used (Wheaton Cat. No. 176780) were made from borosilicate glass formulated to prevent a change of pH and to maintain the purity of the contents. They were prescored to eliminate the need for filing.

The dispensing equipment pumps the solution from the storage vessel and reproducibly injects a pre-set volume into the ampoules, and automatically flame seals the ampoules. Ampoules randomly selected for analysis were also weighed to verify the reproducibility of the filling operation. No significant changes in weight were detected in the four solutions during the filling operation.

The ampoules used for Series 910000 and 920000 were of 10 mL capacity while 20 mL ampoules were used for the Series 930000 and Series 940000 samples. The dispensing equipment was adjusted to deliver 10 mL in the first group. But only about 18.4 mL could be dispensed into the 20 mL ampoules because delivery of a greater volume resulted in the liquid splashing up onto the neck of the ampoule.

The precision of the ampouling operation is shown by the data in Table 4.

2.4 Numbering Sequence

The ampoules are labeled and numbered in the following sequences:

Series 910000	. . . . .	910001 to 910600
Series 920000	. . . . .	920001 to 920600
Series 930000	. . . . .	930001 to 931200
Series 940000	. . . . .	940001 to 941200

The rationale of the following sequence is illustrated as follows:

910001

First digit: Fiscal Year 1979
Second digit: Sample type 1, 2, 3, or 4
Remaining digits: Sample serial number, e.g., 0001

The samples were replaced in the individually compartmented boxes in which the ampoules were received from the manufacturer. Care was exercised to replace them in the boxes in the order in which they were filled. Samples for measurement were selected from these by a random number process. Altogether, 76 ampoules were selected from each of Series 910000, and Series 920000 for this purpose, while 30 were selected from the Series 930000, and Series 940000. No differences were found in either mass content or composition that could be attributed to sequence of preparation. Accordingly, it is believed that the samples in each series are substantially uniform with respect to composition and total content. See Table 4.

The samples delivered to EPA and USGS were numbered sequentially, ignoring the gaps resulting from removal of the test samples. However, the actual production sequence could be ascertained should the need arise.

2.5 Analysis of Ampoules

Essentially seven ampoules were analyzed for each specific determination. However, for purposes of convenience, all measurements were not made on the same ampoule. The measurement data are summarized in Tables 5, 6, 7 and 8. The methods used for measurement are summarized in the following subsections.

2.5.1. pH Measurements

The pH measurements were made on diluted samples of the concentrate. The combination pH electrode was calibrated with pH 4.01 and 7.00 buffers and the sample readings were taken directly from the digital pH meter display.

2.5.2. Conductivity Measurements

The conductivity measurements were made with a dip type conductivity cell in the A.C. mode at a frequency of 1 kHz. The cell constant was determined using a 0.01 demal solution [Jones and Bradshaw, J. Am. Chem. Soc. 55, 1780 (1933)]. Appropriate temperature corrections were made. The values reported were made at 23 °C.

2.5.3. Acidity Measurements

The acidity content of each ampoule was determined by coulometric titration of hydrogen ion to the designated pH = 8.3.

2.5.4. Determination of Anions

The anions fluoride, chloride, nitrate, and sulfate were determined by ion-chromatography. All four anions were done sequentially with a single injection. Chromatographic conditions were as follows: eluent 0.003 mol/L $NaHCO_3$ and 0.0018 mol/L Na_2CO_3; flow-rate 2 mL/minute; sample loop 100 µL; anion columns 3 x 500 mm plus 3 x 150 mm pre-column; suppressor column 6 x 250 mm. Baseline resolution was obtained for all four anions with a total elution time of 32 minutes. Three calibration standards containing the four anions were prepared encompassing the range of the samples. Quantitation was performed by interpolation of the first order least squares fit of the calibration standards' peak-height response versus concentration. Each ampoule of series 910000 was diluted to 50 mL, and each ampoule of series 920000 to 140 mL. Results have been normalized to a dilution of 500 mL per ampoule.

2.5.5. Analysis for Cations

2.5.5.1. Measurement of Ammonium Ions

The chosen technique consisted of chemical measurement according to the procedure given in the following reference: C. O. Willits, and C. L. Ogg, "1949 Report of Standardization of Microchemical Methods, Micro Kjeldahl Nitrogen Determinations", USDA Eastern Regional Research Laboratory, Philadelphia, PA. A micro-Kjeldahl steam distillation apparatus was used to separate the ammonia, released by sodium hydroxide, which was trapped in boric acid. The ammonia was titrated with standardized 0.01N hydrochloric acid using methyl purple indicator.

2.5.5.2. Metals by Atomic Absorption and Flame Emission Spectrometry

All of the metallic cations were measured by atomic absorption or flame emission spectrometry. Measurements were made both on the bulk solution and on the ampoules. The contents of an ampoule were quantitatively transferred to a 100 mL volumetric flask. After addition of 1 mL of NBS purified hydrochloric acid, the solution was diluted to the calibrated volume. Emission or absorption measurements were made in duplicate. Calibration standards were made by dissolution of pure salts or pure metals.

3. ANALYTICAL RESULTS

The analytical results for Series 910000 and Series 920000 are summarized in Tables 5, and 6. The symbols used are as follows:

n = number of samples analyzed

$$\bar{x} = \frac{x_1 + x_2 + \ldots + x_n}{n}$$

$$s = \left(\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)} \right)^{1/2}$$

The values listed under $\bar{x}$ are the best estimates of various compositional parameters of the solution measured after the contents of each ampoule has been diluted to 500 mL.

The compositional data for Series 930000 and Series 940000 are given in Tables 7, and 8. The values reported here have been determined directly on the samples contained in the 20 mL ampoules without further dilution. The acidity values are based upon combining the contents of two ampoules. The pH and conductivity values are for undiluted samples but of course are independent of the volume of sample measured.

4. DISCUSSION

The samples in each series are believed to be uniform in composition. Every ampoule in each series contains the same amount of liquid within narrow limits. The dilution of the contents should not introduce any errors, provided distilled water is used. The samples can be used to determine the between-laboratories variability within the requirements for precipitation analysis.

5. RE-EXAMINATION OF 1975 SAMPLES

Table 9 shows that there have been no significant changes in the concentrations of the anions.

Most of the cations have remained relatively stable. Copper and lead have decreased significantly, however, as a result of interaction with the walls of the ampoules. Although iron was proposed for the 1975 samples, it was found that it could not be retained at pH 6; it therefore was omitted from this preparation.

In Table 9 under Sample B it is seen that no values for pH and ammonium ion are reported under the 1979 column. In addition, the acidity measurements are missing for this same year. Unfortunately the supply of ampoules retained from 1975 had been exhausted before these measurements could be obtained.

In the re-examination of 1975 samples, the data reported in Table 9 for 1979 were derived from the analysis of at least two ampoules.

6. RE-EXAMINATION OF 1977 SAMPLES

Table 10 shows very few changes in the constituents of the 1977 samples. SO_4 and Ca have increased. Sample 730000 ampoule was rinsed with hydrochloric acid to dissolve the precipitate before analysis of the cations. This resulted in the recovery of the iron that was originally added to the solution, 0.18 mg/L.

The acidity standard Series 740000 has decreased in μeq of acid by 15 percent.

A minimum of two ampoules was used for each determination in 1979 for the re-examination of the 1977 samples.

7. INSTRUCTIONS FOR USE

7.1 Series 910000 and Series 920000

The samples consist of ampoules of concentrations which simulate rainwater, when diluted to 500 mL. The ampoules are pre-scored to facilitate breaking off the top. Glassware should be thoroughly cleaned and rinsed with distilled water before use. The recommended procedure for preparation of the test sample is as follows:

1. Rinse the outside of the ampoule to remove dust and allow to air dry.

2. Hold ampoule in a vertical position, tip over and back, and gently tap to transfer any liquid from the top to the body of the ampoule.

3. Hold ampoule with a paper towel (a precaution to prevent injury to hand) and snap off the top at the scored constriction.

4. Place a clean funnel in the neck of a clean 500 mL volumetric flask and transfer the contents of the ampoule, with gentle shaking as required to facilitate removal of liquid.

5. Rinse the ampoule two times with distilled water and transfer the rinsings to the flask.

6. Add distilled water to the flask to dilute to the calibrated volume and mix contents thoroughly.

7. Treat the resulting solution with the same care and in the same manner as a sample of natural rainwater.

7.2. Series 930000 and Series 940000

The solutions are intended for use without additional dilution.

7.2.1. Acidity Measurement

Empty the contents of two ampoules into a clean 100 mL beaker, according to instructions 1, 2, and 3 in Section 6.1. Hold the inverted ampoule over the beaker until contents have drained as much as possible. Check for visible inclusions of solution in the ampoule and shake again, if required. Any film of solution remaining in the ampoule will not cause significant error.

7.2.2. Conductivity and pH Measurements

Empty the contents of one ampoule into a clean 30 mL beaker. Remove substantially all the contents by shaking. However, the measurements are not influenced by the quantity of sample used, hence quantitative delivery is not required. It is convenient to measure sample conductivity, followed by measurement of pH on the same sample.

8. ACKNOWLEDGEMENTS

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of these reference materials is gratefully acknowledged: T. A. Rush, and G. Marinenko. Mr. R. K. Kirby of the NBS Office of Standard Reference Materials was responsible for overseeing the ampouling and labeling of the samples.

The work was performed for the Environmental Protection Agency under Interagency Agreement EPA-IAG-79-DF0666. Informative discussions with Mr. Vance R. Highsmith, EPA, Project Officer, and Dr. Richard J. Thompson, EMD/EMSL/EPA are gratefully acknowledged.

Table 1. Target Compositions.

Unit of Concentration mg/L

Constituent	Series 910000	Series 920000
pH	--	--
Conductivity	--	--
Acidity	--	--
SO_4	.73*	2.23*
SO_4 (S)	.24	.74
NO_3	.816	2.138
NO_3 (N)	.182	.483
NH_4	.208	.651
NH_4 (N)	.161	.506
Cl	.810	3.020
F	.143	.238
Ca	.200	.545
Cd	.049	.225
Cu	.070	.287
K	.146	.488
Mg	.050	.200
Mn	.037	.151
Na	.226	.455
Ni	.059	.176
Pb	.062	.207
Zn	.065	.392
Fe	.032	.072

*The values shown were adjusted after a telephone conversation between Dr. Robert W. Burke, NBS, and Dr. R. J. Thompson, EPA.

Table 2. Chemicals Used for Preparation of Reference Materials.

Chemical	Formula	Source
Calcium Chloride	$CaCl_2 \cdot 2H_2O$	Mallinckrodt Analytical Reagent
Magnesium Sulfate	$MgSO_4 \cdot 7H_2O$	E & A Tested Purity
Zinc Nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	Baker Analyzed
Cadmium Nitrate	$Cd(NO_3)_2 \cdot 4H_2O$	Fisher Analyzed
Cupric Chloride	$CuCl_2 \cdot 2H_2O$	B & A Reagent
Cupric Nitrate	$Cu(NO_3)_2 \cdot 3H_2O$	Baker Analyzed
Nickel Nitrate	$Ni(NO_3)_2 \cdot 6H_2O$	Mallinckrodt Analytical Reagent
Lead Acetate	$Pb(Ac)_2 \cdot 3H_2O$	Baker Analyzed
Manganese Chloride	$MnCl_2 \cdot 4H_2O$	B & A Reagent
Ammonium Chloride	NH_4Cl	Baker Analyzed
Sodium Chloride	NaCl	Mallinckrodt Analytical Reagent
Sodium Fluoride	NaF	Fisher Certified
Sodium Nitrate	$NaNO_3$	Baker Analyzed
Potassium Nitrate	KNO_3	Baker Ultrex
Ferric Ammonium Citrate		Fisher Purified
Citric Acid Monohydrate		Baker Analyzed

Table 3. Recipe for NBS Precipitation Reference Materials, III.

Preparation of Stock Solutions (10 liters)

Chemical	910000	920000
H_2SO_4 (μeq)	5,600	15,000
NH_4Cl (gm)	.3080	.9650
$CaCl_2 \cdot 2H_2O$ (gm)	.3676	1.0000
NaCl (gm)		.2150
$NaNO_3$ (gm)	.1000	
NaF (gm)	.1575	.2625
$Cd(NO_3)_2 \cdot 4H_2O$ (gm)	.0675	.3084
$Cu(NO_3)_2 \cdot 3H_2O$ (gm)	.1335	
$CuCl_2 \cdot 2H_2O$ (gm)		.3850
KNO_3 (gm)	.1894	.6315
$MgSO_4 \cdot 7H_2O$ (gm)	.2520	1.0086
$MnCl_2 \cdot 4H_2O$ (gm)	.0660	.2720
$Ni(NO_3)_2 \cdot 6H_2O$ (gm)	.1450	.4366
$Pb(Ac)_2 \cdot 3H_2O$ (gm)	.0570	.1896
$Zn(NO_3)_2 \cdot 6H_2O$ (gm)	.1480	.8926
Ferric Ammonium Citrate (gm)	.0923	.2076
Citric Acid Monohydrate (gm)	.8406	3.3622

Table 4. Precision of Ampouling.

Series	n	$\bar{x}$,g	s
910000	12	9.962	0.018
920000	12	9.972	0.018
930000	12	18.30	0.022
940000	10	18.39	0.016

To demonstrate that there is no systematic trend in the sampling operations, randomly selected ampoules and the weights of liquid obtained for the 920000 Series are given below:

Random Ampoules Listed Numerically	Ampoules in Order of Weighing	Weight of Liquid, grams
1	1	9.9986
80	11	9.9988
145	5	9.9612
240	4	9.9600
289	9	9.9518
368	7	9.9578
433	10	9.9605
528	3	9.9572
577	2	9.9537
672	8	9.9824
721	6	9.9825
816	12	9.9948

Compositional results in Tables 5 and 6 likewise show no systematic trend.

Table 5. Analytical Data for Series 910000.

Constituent	Unit	n	$\bar{x}$	s
pH		7	5.03	0.24
Conductivity	$\mu S.cm^{-1}$	7	13.20	.08
Acidity	µeq/amp*	7	17.38	.45
SO_4	mg/L	7	.779	.008
SO_4 (S)	mg/L	7	.260	.003
NO_3	mg/L	7	.826	.002
NO_3 (N)	mg/L	7	.186	.0005
NH_4	mg/L	7	.214	.010
NH_4 (N)	mg/L	7	.166	.008
Cl	mg/L	7	.908	.008
F	mg/L	7	.154	.002
Ca	mg/L	7	.248	.0014
Cd	mg/L	7	.051	.0004
Cu	mg/L	7	.073	.0003
K	mg/L	7	.156	.001
Mg	mg/L	7	.056	.0006
Mn	mg/L	7	.038	.0006
Na	mg/L	7	.284	.0050
Ni	mg/L	7	.061	.0003
Pb	mg/L	7	.070	.0006
Zn	mg/L	7	.066	.0006
Fe	mg/L	7	.030	.0006

*ampoule

Table 6. Analytical Data for Series 920000.

Constituent	Unit	n	$\bar{x}$	s
pH		7	4.35	0.12
Conductivity	$\mu S \cdot cm^{-1}$	7	43.49	.08
Acidity	μeq/amp*	7	66.02	.75
SO_4	mg/L	7	2.349	.024
SO_4 (S)	mg/L	7	.776	.008
NO_3	mg/L	7	2.147	.006
NO_3 (N)	mg/L	7	.485	.001
NH_4	mg/L	7	.660	.013
NH_4 (N)	mg/L	7	.514	.010
Cl	mg/L	7	3.274	.014
F	mg/L	7	.256	.003
Ca	mg/L	7	.654	.0048
Cd	mg/L	7	.224	.0034
Cu	mg/L	7	.294	.0019
K	mg/L	7	.506	.0074
Mg	mg/L	7	.226	.0026
Mn	mg/L	7	.154	.0006
Na	mg/L	7	.558	.0078
Ni	mg/L	7	.185	.0010
Pb	mg/L	7	.214	.0070
Zn	mg/L	7	.402	.0042
Fe	mg/L	7	.071	.0019

*ampoule

Table 7. Compositional Data for Series 930000.

Constituent	Unit	n	$\bar{x}$	s
pH		9	3.91	.025
Conductivity	$\mu S \cdot cm^{-1}$	7	69.12	.20
Acidity	µeq/2 amp*	7	5.90	.24

*ampoules

Table 8. Compositional Data for Series 940000

Constituent	Unit	n	$\bar{x}$	s
pH		10	3.62	0.015
Conductivity	$\mu S \cdot cm^{-1}$	7	121.44	.22
Acidity	μeq/2 amp*	7	9.98	.40

*ampoules

Table 9. Re-examination of 1975 Samples.

Constituent	Unit	A			B		
		1975	1977	1979	1975	1977	1979
pH		6.18			6.15		
Conductivity	$\mu S \cdot cm^{-1}$	5.8		5.10	18.3		17.15
Acidity	μeq/amp*	4.9			5.0		
SO_4	mg/L	1.08	1.09	1.12	3.57	3.81	3.77
SO_4 (S)	mg/L	.361	.365	.373	1.19	1.27	1.26
NO_3	mg/L	.115	.146	.111	.664	.700	.674
NO_3 (N)	mg/L	.026	.033	.025	.150	.158	.152
NH_4	mg/L	.109		.08	.49		
NH_4 (N)	mg/L	.089		.06	.38		
Cl	mg/L	.106		.128	1.25		1.08
F	mg/L	.102		.108	.096		.097
Ca	mg/L	.099	.084	.100	.442	.370	.388
Cd	mg/L	.030	.030	.032	.116	.115	.096
Cu	mg/L	.052	.040	.033	.088	.035	.020
K	mg/L	.063	.066	.067	.102	.107	.103
Mg	mg/L	.086	.086	.087	.456	.454	.396
Mn	mg/L	.052	.054	.052	.081	.085	.070
Na	mg/L	.153	.166	.166	.516	.546	.488
Ni	mg/L	.021	.022	.021	.104	.113	.087
Pb	mg/L	.018	.009	.010	.088	.058	.070
Zn	mg/L	.021	.020	.020	.095	.089	.064
Fe	mg/L	---	---	---	---	---	---

*ampoule

Table 9. Re-examination of 1975 Samples. (continued)

		C			D		
Constituent	Unit	1975	1977	1979	1975	1977	1979
pH		6.20		5.75	6.07		5.78
Conductivity	$\mu S \cdot cm^{-1}$	59.8		57.02	117		112
Acidity	µeq/amp*	25			47		
SO_4	mg/L	5.01	5.01	4.79	10.0	9.90	9.80
SO_4 (S)	mg/L	1.67	1.67	1.60	3.33	3.30	3.27
NO_3	mg/L	6.64	6.64	6.64	10.89	10.89	10.95
NO_3 (N)	mg/L	1.50	1.50	1.50	2.46	2.46	2.47
NH_4	mg/L	2.46		2.48	4.63		4.61
NH_4 (N)	mg/L	1.91		1.93	3.60		3.59
Cl	mg/L	7.63		7.69	17.79		18.96
F	mg/L	.195		.184	.296		.289
Ca	mg/L	1.23	1.04	1.21	2.84	2.42	2.80
Cd	mg/L	.578	.576	.564	1.01	0.99	.99
Cu	mg/L	.200	.104	.088	.393	.174	.157
K	mg/L	1.01	1.01	1.04	3.06	2.92	3.24
Mg	mg/L	.729	.712	.720	.922	.936	.906
Mn	mg/L	.100	.103	.098	.200	.204	.202
Na	mg/L	2.46	2.54	2.58	5.44	5.46	5.72
Ni	mg/L	.506	.560	.522	1.01	1.03	1.05
Pb	mg/L	.152	.105	.124	.110	.062	.074
Zn	mg/L	.307	.284	.304	.610	.626	.612
Fe	mg/L	---	---	---	---	---	---

*ampoule

Table 10. Re-examination of 1977 Samples.

Constituent	Unit	710000		720000		730000	
		1977	1979	1977	1979	1977	1979
pH		4.48	4.25	4.08	4.07	5.98	5.86
Conductivity	$\mu S \cdot cm^{-1}$	28.84	30.89	77.9	84.4	190.5	205.2
Acidity	µeq/amp*	37.57	30.06	59.94	53.69	52.5	39.80
SO_4	mg/L	2.66	3.25	7.90	9.96	9.94	10.0
SO_4 (S)	mg/L	.89	1.08	2.64	3.32	3.32	3.33
NO_3	mg/L	.503	.53	3.02	3.18	14.50	15.3
NO_3 (N)	mg/L	.114	.120	.68	.72	3.27	3.45
NH_4	mg/L	.107	.115	1.07	1.08	10.18	10.14
NH_4 (N)	mg/L	.084	.089	.82	.82	7.93	7.89
Cl	mg/L	1.35	.961	7.22	7.75	42.4	48.72
F	mg/L	.046	.039	.0997	.087	.103	.093
Ca	mg/L	.0766	.089	.766	.844	5.98	7.14
Cd	mg/L	.0230	.022	.0572	.056	.114	.113
Cu	mg/L	.0360	.034	.192	.204	1.012	1.02
K	mg/L	.199	.206	.994	1.016	4.94	5.18
Mg	mg/L	.110	.111	1.12	1.14	--	--
Mn	mg/L	.0296	.029	.0586	.058	.0846	.083
Na	mg/L	.151	.169	2.86	2.82	9.66	10.1
Ni	mg/L	.0338	.031	.0948	.091	.518	.518
Pb	mg/L	.0232	.023	.0988	.101	1.04	1.14
Zn	mg/L	.0344	.034	.198	.202	1.05	1.04
Fe	mg/L	.0214	.022	.0612	.068	.076	.163

*ampoule

Table 10. Re-examination of 1977 Samples. (continued)

740000

Constituent	Unit	1977	1979
pH		3.81	4.02
Conductivity	$\mu S \cdot cm^{-1}$	80.0	--
Acidity	µeq/amp*	9.32	7.96

*ampoule